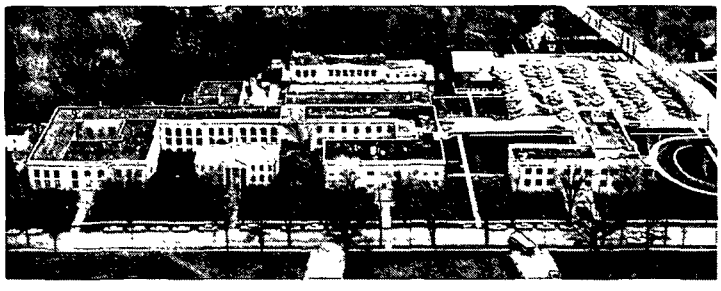

THE INSTITUTE OF PAPER CHEMISTRY, APPLETON, WISCONSIN

IPC TECHNICAL PAPER SERIES
NUMBER 75

THE EFFECT OF SHEET STRUCTURE AND COMPOSITION ON THE X–BAND DIELECTRIC CONSTANTS OF WATER–PAPER MIXTURES

CHARLES C. HABEGER AND GARY A. BAUM

FEBRUARY, 1979

The effect of sheet structure and composition on the X-band dielectric constants of water-paper mixtures

Charles C. Habeger, and Gary A. Baum

The Institute of Paper Chemistry, Box 1039, Appleton, Wis. 54912

KEYWORDS: Dielectric constant; Wet pressing; Water; Microwaves; Basis weight; Paper; Refining; TiO_2; Mixtures; Calendering; Temperature

Abstract

A precise technique for determining microwave dielectric constants from slotted line measurements is adapted to paper samples. The effects of refining, wet pressing, calendering, and TiO_2 addition on the dielectric constant *vs.* moisture curves are reported and discussed. The observed in-plane dielectric anisotropy is discussed. The importance of considering geometry at the fiber level in explanations of the dielectric behavior of paper is stressed.

This paper has been submitted for publication in Tappi.

Introduction

Below microwave frequencies water has a large, real dielectric constant ($\sim$80). This is due to the motion of its permanent molecular dipole moment. At low frequencies the dipoles can oscillate in phase with the changing direction of the electric field, thereby contributing to the real part of the dielectric constant. As the microwave range is approached, however, the dipoles are unable to stay in phase with the electric field, and both the real and imaginary parts of the dielectric constant are large. At higher frequencies the permanent dipoles cannot contribute, and the dielectric constant of water decreases to about 5.

The permanent dipole moment of water is the dominant factor in the interaction between paper-water mixtures and microwave radiation. Microwave moisture gages, which exploit this fact, are used extensively in the paper industry. Microwave driers, which depend on the strong absorption of microwave radiation by water, have also found applications in the manufacture of paper. A microwave moisture gage measures the effect that a sample has on a microwave signal in a particular configuration. The response is a function (different for each instrument) of the paper's

effective complex dielectric constant and geometry. The moisture content is determined by calibrating the instrument response to the actual moisture content, as measured gravimetrically.

There is a good deal of data concerning the effects of sheet composition and structure on the calibration curves for particular instruments (1). However, few measurements have been made in terms of the basic parameters, i.e., the effective complex dielectric constant of the sheet. Although dielectric constant data for paper have been reported (2-5), we were not able to find any information concerning the relationship of dielectric constant vs. moisture curves to papermaking parameters. This type of information would be useful to manufacturers in designing instruments which are less sensitive to changes in the paper manufacturing process. Also, it should be helpful to the user in estimating instrument limitations.

In this article we report the results of experiments designed to determine the effects of some papermaking parameters on the X-band dielectric constant of paper-water mixtures. These parameters are refining, calendering, wet pressing, basis weight, and TiO_2 content. The influence of temperature and the electric field orientation with respect to the machine direction of the paper are also investigated. The experiments are conducted in the low (<14%) moisture content range.

Experimental

The change in the dielectric constant vs. moisture curves caused by papermaking parameter changes can be small. Therefore, we needed an apparatus that could measure the dielectric constant of thin sheets with

good accuracy and sensitivity. Accordingly, we adapted an established technique which uses a statistical analysis of slotted line data for measurements on thin sheets. The system, described below, is quite sensitive. The frequency range is limited to the X-band (8.2 to 12.4 GHz).

A schematic diagram of the experimental apparatus used in this work is shown in Fig. 1. The permittivity of a paper specimen is determined from its effect on the standing wave pattern in the shorted waveguide. The sample is placed in the waveguide with its face normal to the microwave radiation, between the moveable short and the slotted waveguide. The moveable short is attached to a precision micrometer, as is the detector probe in the slotted line. Energy is supplied to the waveguide by a Polarad 1108A variable frequency microwave signal generator, with internal 1 kHz square wave amplitude modulation, after passing through a Hewlett Packard 11686 A low pass filter. The signal is picked up by the probe, rectified by an Alpha Industries DDC4561D Low Barrier Schottky Diode (LBSD) in the probe mount, and sent to a Hewlett Packard 415E Standing Wave Ratio (SWR) meter which has a 1 kHz bandpass filter. It was necessary to modify the probe carrier and moveable short in order to use micrometers with 0.0001 inch dial divisions. These micrometers were necessary to provide the accuracy needed when working with thin sheets.

[Fig. 1 here]

The signal detected by the probe results from interference between traveling waves moving toward and away from the sample. The wave pattern can be defined by using the probe to find the location of a standing wave node and the standing wave ratio (SWR). The reflection

coefficient, Γ, can be calculated from this information. The reflection coefficient is defined at a plane in the waveguide as the complex ratio of the reflected to the incident wave.

If the shorted waveguide is empty (no sample in place), a near perfect standing wave results from the interference between the incoming wave and the wave reflected by the short. The absolute value of Γ is one at all points along the waveguide, while its phase angle varies from π at the nodes to zero at the antinodes. If N measurements of Γ were made at some point as the short was moved through distances, $\underline{d} = \underline{j}\lambda/2N$, where $\underline{j} = 0, \ldots, N-1$ and λ is the signal wavelength, the values of Γ, when plotted in the complex plane, would lie on the unit circle $2\pi/N$ radians apart. If a sheet of paper is inserted in the waveguide between the detector and the short, radiation reflected and absorbed by the sheet will rotate the Γ's and move them inside the unit circle. The N values of Γ now lie on a new circle, but they are not $2\pi/N$ radians apart.

The effect of a substance in a waveguide may be characterized at some plane by a scattering matrix, $\underline{S}_{\underline{ij}}$, where $\underline{i},\underline{j} = 1,2$. The scattering matrix is the ratio (at a defined plane) between radiation entering the substance on the $\underline{j}$-side and exiting from the $\underline{i}$-side, when the waveguide is terminated in its characteristic impedance on the $\underline{i}$-side. Deschamps (6) has developed a method to graphically determine the scattering matrix at a plane a known distance from the first short location, using the N values of Γ. A clear explanation of this procedure is provided by Altschuler (7).

In order to calculate $\underline{S}_{ij}$ for paper samples, we have programmed a computer to do calculations equivalent to Deschamps' graphical method. Only four values of Γ are needed to compute the scattering matrix. However, in order to get reasonable statistics and yet avoid making the data gathering too time consuming, we used N = 8. An estimate of the probable error is made from the scatter in the calculated values of $\underline{S}_{ij}$ resulting from taking different combinations of the measured Γ's.

For a homogeneous material of known dimension, it is possible to calculate the complex dielectric constant from the scattering matrix if either the sheet thickness or the distance of the sheet from the reference plane is known. Unfortunately, paper is a very inhomogeneous material with a poorly defined thickness. Nonetheless, if the paper's measured scattering matrix can be reproduced by a homogeneous sheet of constant thickness, a dielectric constant can be associated with the paper. This is possible if $|\underline{S}_{11}| = |\underline{S}_{22}|$. In this case the dielectric constant of the paper can be said to equal that of the fictitious homogeneous sheet. In order to determine a unique dielectric constant from the scattering matrix, a knowledge of either the sheet thickness or boundary location is necessary. Paper caliper and boundary location are nebulous concepts, and the value of the dielectric constant determined by this approach will be no better than the number ascribed to either one of these.

For purposes of data collection, we used the constrained thickness technique. The thickness is determined using a standard caliper gage. The advantages of this method (as compared to the constrained boundary method) are that (1) the sheet boundary area is not deformed, and (2)

the initial short position can be chosen so that the sample is never too close to a waveguide null where the effect of the paper is small and difficult to measure.

Using the technique just described, there are three ways to evaluate the quality of the data. These are: (1) scatter in the dielectric constant; (2) the difference between the absolute values of $\underline{S}_{11}$ and $\underline{S}_{22}$; and (3) the difference between the distance from the sheet to the first short location as measured and as calculated by the computer. Large values for any of these numbers indicate poor data and can arise from a number of sources, e.g., poor data taking, sample misalignment, the sheet being drier when it is near an antinode than when it is near a node, and imperfections in the waveguide. The experiments are repeated if any of these numbers are considered excessive.

The method for mounting the sheets inside the waveguide deserves special mention. In order to obtain accurate and repeatable results, it is necessary to carefully align the paper in the waveguide without inserting extraneous materials that can alter the standing wave pattern. This was achieved in the present work by supporting the samples in "window shims" of the appropriate thickness. A window shim has a punched hole with a height equaling that of the waveguide (0.4 inch), with a length slightly longer than the waveguide width (0.9 inch), and a thickness slightly less than the thickness of the specimen to be supported. The paper specimen is cut to fit tightly in the window shim. The shim is clamped between the slotted line and the moveable short. There is no first effect on the standing wave pattern due to the shim, because the currents in the waveguide are parallel to the wall gaps caused by the shim.

For thin sheets (<0.012 inch) the effect of the paper on the standing wave pattern is not large enough to allow accurate measurements of the dielectric constant. From measurements made on stacks of different thicknesses, however, it was found that the variation of the calculated dielectric constants was within the expected experimental error. If sheets are carefully cut and stacked in the window shim, therefore, measurements on stacks of thin sheets can be used to calculate accurate dielectric constants.

Altogether, the slotted line technique, careful specimen mounting procedures, and computer simulation of the graphical method for analyzing the slotted line data, have resulted in a system which is capable of high accuracy. The estimated uncertainty in the dielectric constant measurements is ±0.05.

General comments

Paper can be thought of as a heterogeneous mixture of air and moist fiber. If paper is viewed as a two component mixture of dielectrics, two changes must be made in the model as the moisture level increases. The dielectric constant of the fiber portion of the mixture must be increased due to the greater concentration of water in the fiber, and the volume percentage of fiber must be increased due to swelling. The effect of both of these mechanisms on the effective dielectric constant of the sheet is strongly dependent on the geometry of the mixture at the fiber level.

Figure 2 demonstrates the importance of geometry on the relationship between the effective dielectric constant of a mixture, ε_e, and the

dielectric constant of the solid fraction, ε_f. Curves are drawn for three geometries; the two extremes of parallel and series alignment and an intermediate geometry of spherical inclusions [Maxwell-Garnett relationship (8)]. All three mixtures are assumed to be 50% vacuum. Figure 3 demonstrates the effect of geometry on the relationship between ε_e and the volume fraction of material, q, with dielectric constant $\varepsilon_f = 30$. The same three geometries are shown. From these two figures it is clear that the geometry at the fiber level must be considered when relating the effective dielectric constant of paper to the dielectric properties of its constituents.

[Figs. 2 and 3 here]

Anisotropy in the geometry of a mixture will result in anisotropy in the dielectric constant. This is easily seen for the simple case of a series mixture which becomes a parallel mixture by rotating the electric field 90°. In paper the fibers can be preferentially aligned in the machine direction. This means that the fiber regions are more contiguous (more like parallel capacitors) along the electric field when the field is aligned with the machine direction than when it is aligned with the cross direction. The effective dielectric constant, therefore, would be expected to be greater in the machine direction.

Another factor that might be important in characterizing the microwave dielectric properties of water-paper mixtures is the different polarizabilities of "bound" and "free" water. There is reason to believe that in cellulose and other materials the oscillation of sorbed water in

an electric field is inhibited. For proteins (9), this results in the motion of the bound water relaxing out at lower frequencies (∿1 GHz) than that portion of water that is free (∿22 GHz). In paper, the increase in the portion of free water at higher moisture contents could be reflected in the dielectric constant vs. moisture curves. In addition, it is possible that the average polarizability of sorbed water molecules may depend on the alignment of the electric field with the fiber. This would be due to anisotropy in the fiber at the molecular level. This (along with anisotropy in the geometry at the fiber level) could cause anisotropy in the effective dielectric constant of the sheet. In light of these statements concerning geometry, we must caution against any approach that does not consider fiber geometry when relating the dielectric constant of paper to the polarizabilities of its constituents.

Results and discussion

All experiments were carried out in a controlled environment, with the specimens conditioned in this environment for at least 12 hours prior to testing. For the changing moisture content studies, the specimens were conditioned, weighed, and measured at relative humidities ranging from 15 to 90%. Ovendry weights were obtained by drying 12 hours in a circulating air oven maintained at 105°C.

Figure 4 shows the effect of moisture content on the real and imaginary parts of the dielectric constant of a 65 g/m^2 newsprint handsheet. The general concave upward form of these curves is exhibited in the results for all samples. This might be due to the increase in the free water percentage as the moisture level increases or an increasingly

connected geometry caused by fiber swelling (see Fig. 3). In either case, the geometry must be considered in any quantitative description of the phenomena.

[Fig. 4 here]

Figure 5 demonstrates the result of measuring the in-plane dielectric constants at various orientations between the machine direction and electric field direction for a 52 g/m^2 machine-made newsprint. We attribute the dielectric anisotropy to the preferential alignment of fibers in the machine direction. Dried-in stresses, which can have a large influence on the anisotropy of elastic coefficients, should not significantly affect the dielectric anisotropy.

[Fig. 5 here]

Experiments at 100°F showed that both the real and imaginary parts of the dielectric constant increased with temperature. The influence of temperature on the dielectric properties of mixtures containing sorbed water is quite complicated, and we will not attempt to explain this trend here.

The dielectric constant is a bulk property of a material, and thus it should not be well correlated with basis weight. We determined the dielectric constant vs. moisture curves for four newsprint handsheet samples differing in basis weight. The effect of basis weight at low moistures is undetectable. The data at the highest moistures, however, show a small increase of dielectric constant with basis weight.

The increase in dielectric constant due to wet pressing, refining, and calendering, is demonstrated in Figs. 6-8, respectively. The samples used for the wet pressing and refining studies were unbleached kraft handsheets prepared with a nominal basis weight of 200 g/m^2. A series of 60 g/m^2 bleached kraft handsheets was used for the calendering work. All three of these papermaking processes increase the sheet density. In general, a density increase results in a tighter packing of dipoles, and thus, a larger dielectric constant. In order to estimate the effect of increasing density, the paper was modeled as a two-phase dielectric mixture of wet fiber and air. For the sake of mathematical simplicity, the sheet geometry is approximated as spherical air inclusions in a fiber matrix (e.g., see Fig. 2). The dielectric constant of the sheet, ε, can then be related to the fiber dielectric constant, $\varepsilon_{\underline{f}}$, and $\underline{q}$, the volume fraction of air, by the Maxwell-Garnett equation (8):

$$(2\varepsilon_{\underline{f}} + 1)(\varepsilon_{\underline{f}} - \varepsilon) = \underline{q}(\varepsilon_{\underline{f}} - 1)(\varepsilon + 2\varepsilon_{\underline{f}})$$

Knowing the fiber density, $\underline{q}$ can be calculated from the measured values of basis weight and caliper. Using this equation, the dielectric constants of the denser sheets can be estimated from the measured dielectric constant of the least dense sheet, as follows. A value for the fiber density is assumed and the $\underline{q}$ of the low density sheet is calculated. The value of $\varepsilon_{\underline{f}}$ is calculated by the Maxwell-Garnett equation using $\underline{q}$ and the measured value of ε. The $\underline{q}$ of the higher density sheet is now calculated and the ε of the higher density sheet is found from the Maxwell-Garnett equation, using the $\varepsilon_{\underline{f}}$ calculated above. These calculations were performed for the UK205 series of samples and the results are included in Figs. 6 and 7, depicting the wet pressing and refining results, respectively. The

calculated dielectric constants at each moisture agree quite favorably with the measured values, except at the highest moisture, where the calculated values fall beneath the measured. The fiber density assumed was 1.6 g/cm^3, although the calculated values were relatively insensitive to fiber density in the range 1.3 to 1.7 g/cm^3.

[Figs. 6, 7 and 8 here]

The generally good agreement between the predicted and measured dielectric constants is taken as evidence that the dielectric effect of wet pressing and refining is basically to change the volume fraction of air. It should be mentioned that the Maxwell-Garnett equation requires values of q small enough that connected inclusions are not occurring. This may not be the case here, where the calculated q's are in the range of 50%, assuming a fiber density of 1.6 g/cm^3.

The comparisons of the calculated and measured dielectric constants for the calendered samples (Fig. 8), however, were not so good (not shown). In this case the predicted values were considerably larger than the measured ones. If the bleached kraft samples are representative of what occurs during the calendering process, the poor agreement suggests that something other than a simple density change is occurring.

Figure 9 demonstrates the effect of a TiO_2 filler on the dielectric constant. Since the real part of the effective dielectric constant of TiO_2 (approximately 117) is larger than that of water (approximately 80), a significant increase in ε' is expected with the addition of TiO_2. The observed increase in ε', however, is small when compared to that caused by an equal volume of water. Perhaps the reason for this is that the TiO_2

exists as isolated "clumps" on the fiber, causing a smaller effect than the water which is distributed in a more connected fashion.

[Fig. 9 here]

The Maxwell-Garnett equation can also be used to estimate the effect of TiO_2 addition on the dielectric constant. This was done by assuming that TiO_2 can be represented as spherical inclusions randomly distributed in a matrix which has the dielectric properties of the unfilled sheet (see Fig. 9). Doping a sheet with spherical inclusions is not an effective way to change dielectric constant, and it is expected that the Maxwell-Garnett equation should underestimate the effect of the TiO_2. The observed change in ε', however, is even less than that predicted by the theory, and ε'' shows a slight negative trend.

Acknowledgments

Dave Brennan gathered the data and John Bachhuber programmed the computer.

Literature cited

1. American Paper Institute Instrumentation Program, Report No. 42, Part VII, Feb. 13, 1978 and Part XI, Sept. 15, 1978.

2. Kumar, A. and Smith, D., Tappi 59(1):149(1976).

3. Chene, M., Revol, N., Pellissier, S., and Mesharo, G., Cellulose Chem. Technol. 1:597(1967).

4. Dusoiu, N., Balanescu, G., and Liviu, T., Celuloza Hirtie 25(2):57(1976).

5. M'Baye, K. and Pellissier, J., Revue ATIP 29(2):51(1975).

6. Deschamps, G., J. Appl. Phys. 24:1046(1953).

7. Felsen, L. Handbook of Microwave Measurements. Chap. IV, Vol. I. (Sucher, M. and Fox, J., eds.), Polytechnic Press, 1963.

8. Maxwell-Garnett, J. C., Philos. Trans. R. Soc. (London) 203:385(1904); 205:237(1906).

9. Pennock, B. and Schwan, H., J. Phys. Chem. 73(8):2600(1969).

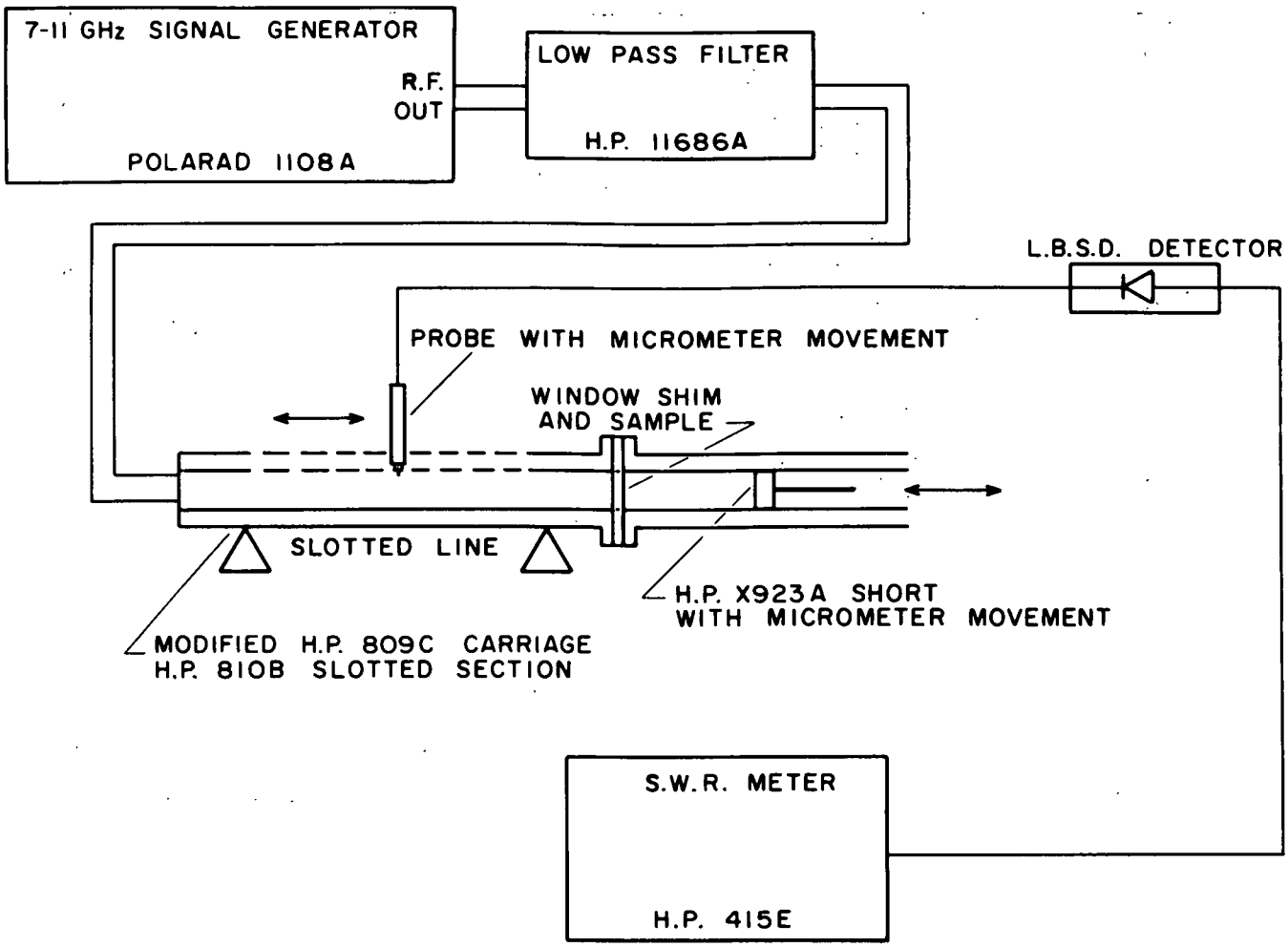

Fig. 1. Schematic of experimental apparatus.

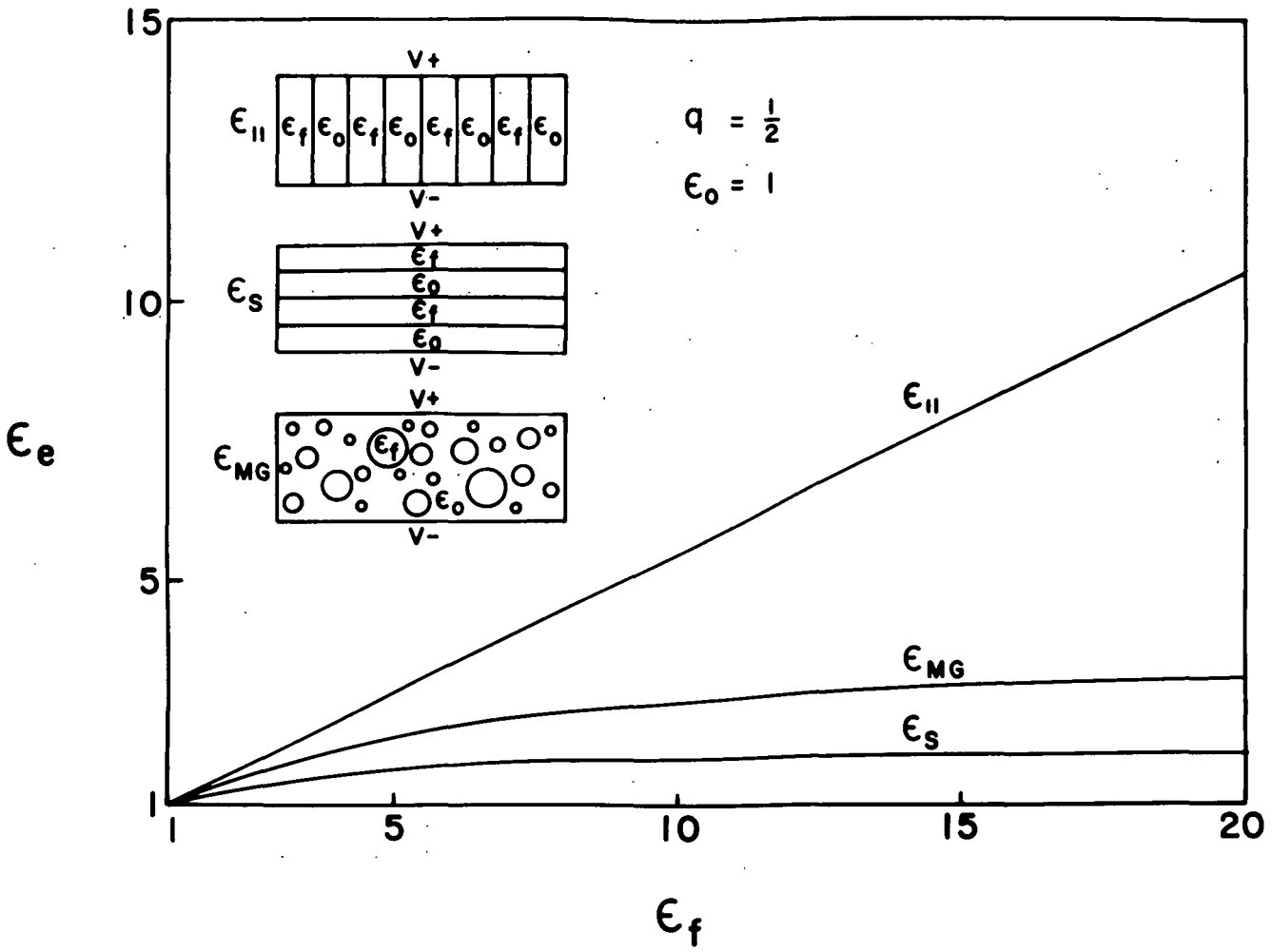

Fig. 2. The effect of geometry on the plot of the effective dielectric constant, ϵ_e, of a vacuum-matter mixture versus the dielectric constant, ϵ_f, of the matter.

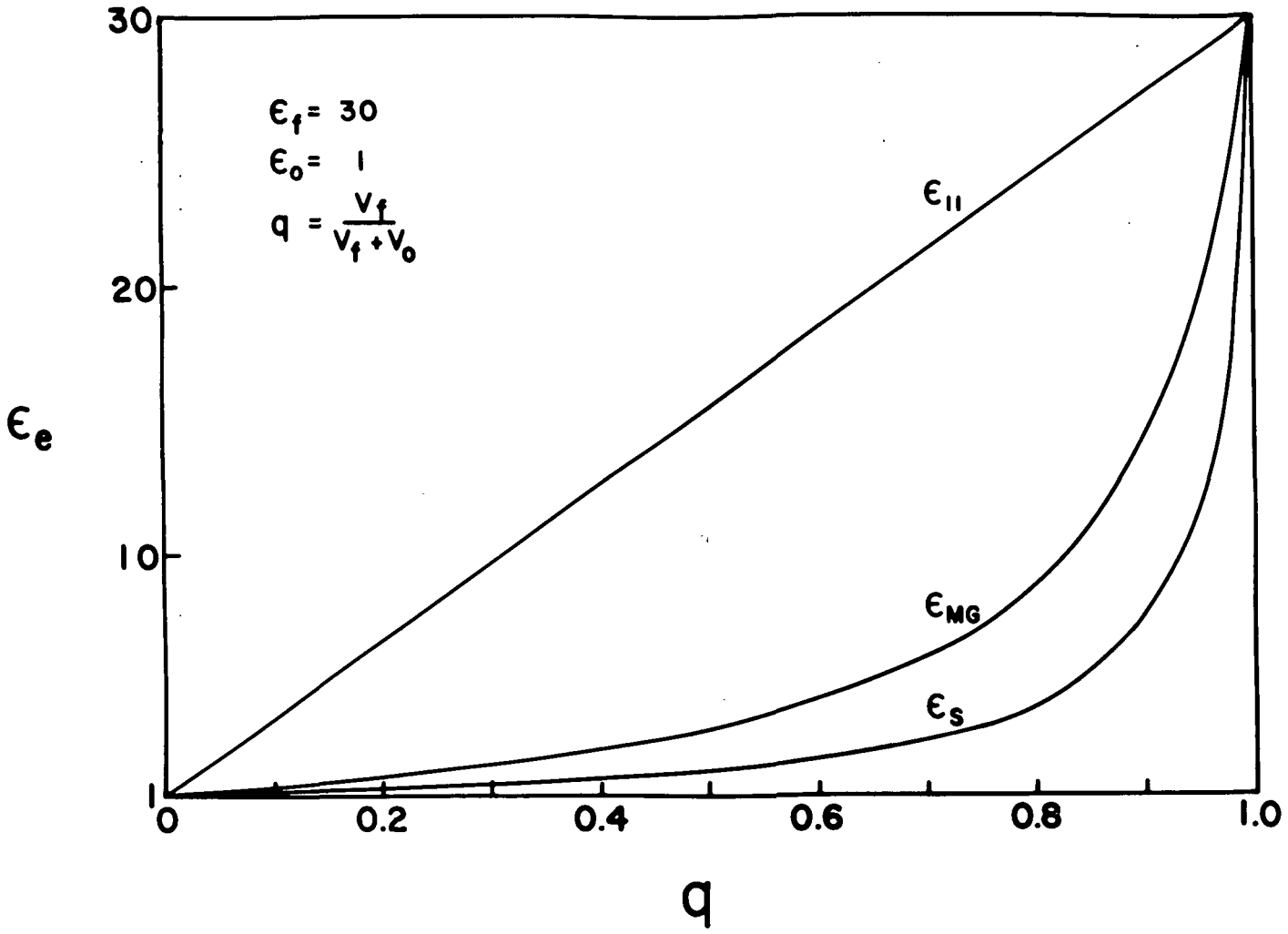

Fig. 3. Plots of the effective dielectric constant, ϵ_e, of a vacuum-matter mixture as a function of the volume fraction, q, of matter for different mixture geometries.

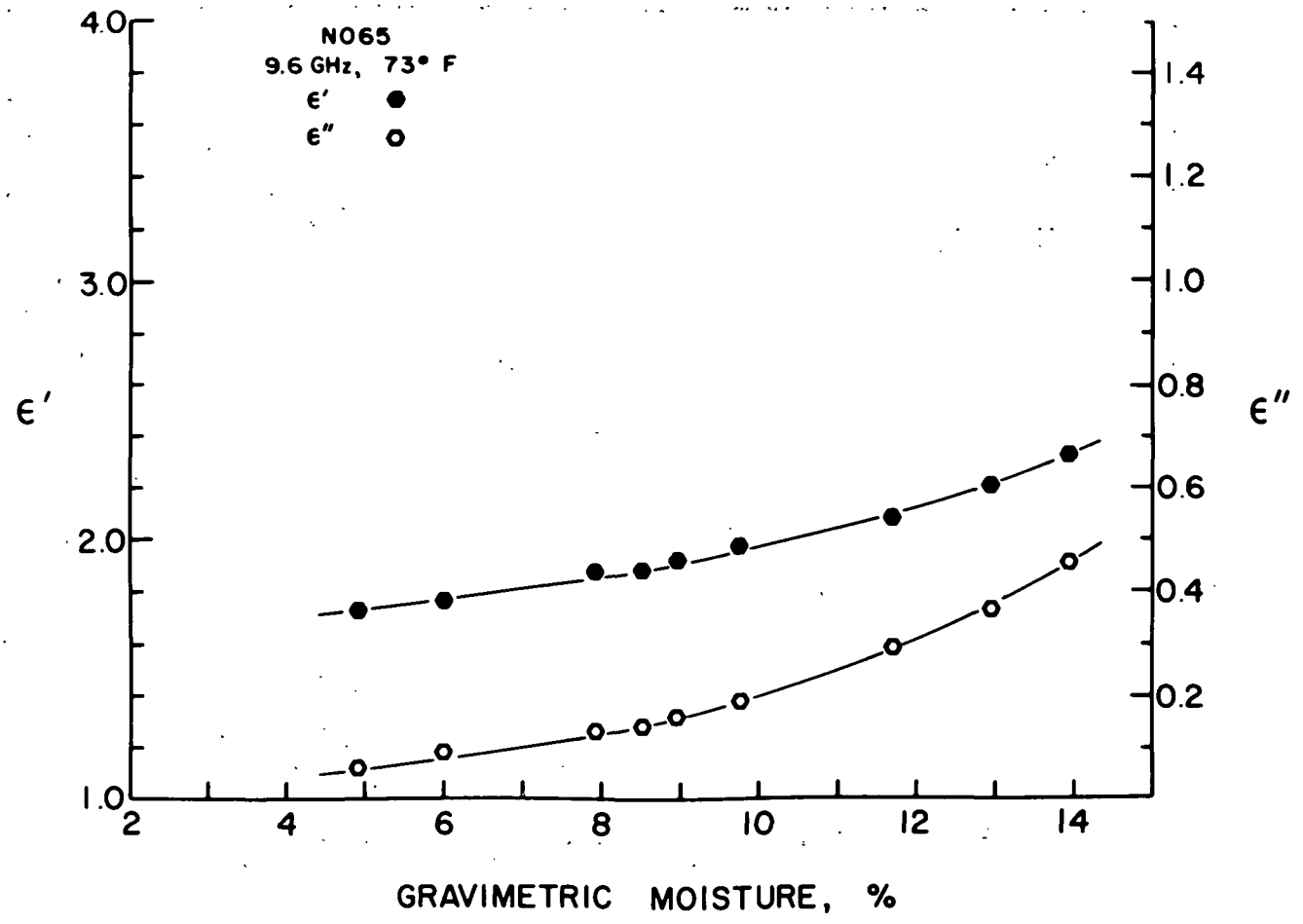

Fig. 4. Dielectric constant versus gravimetric moisture for a 62 g/m^2 newsprint handsheet.

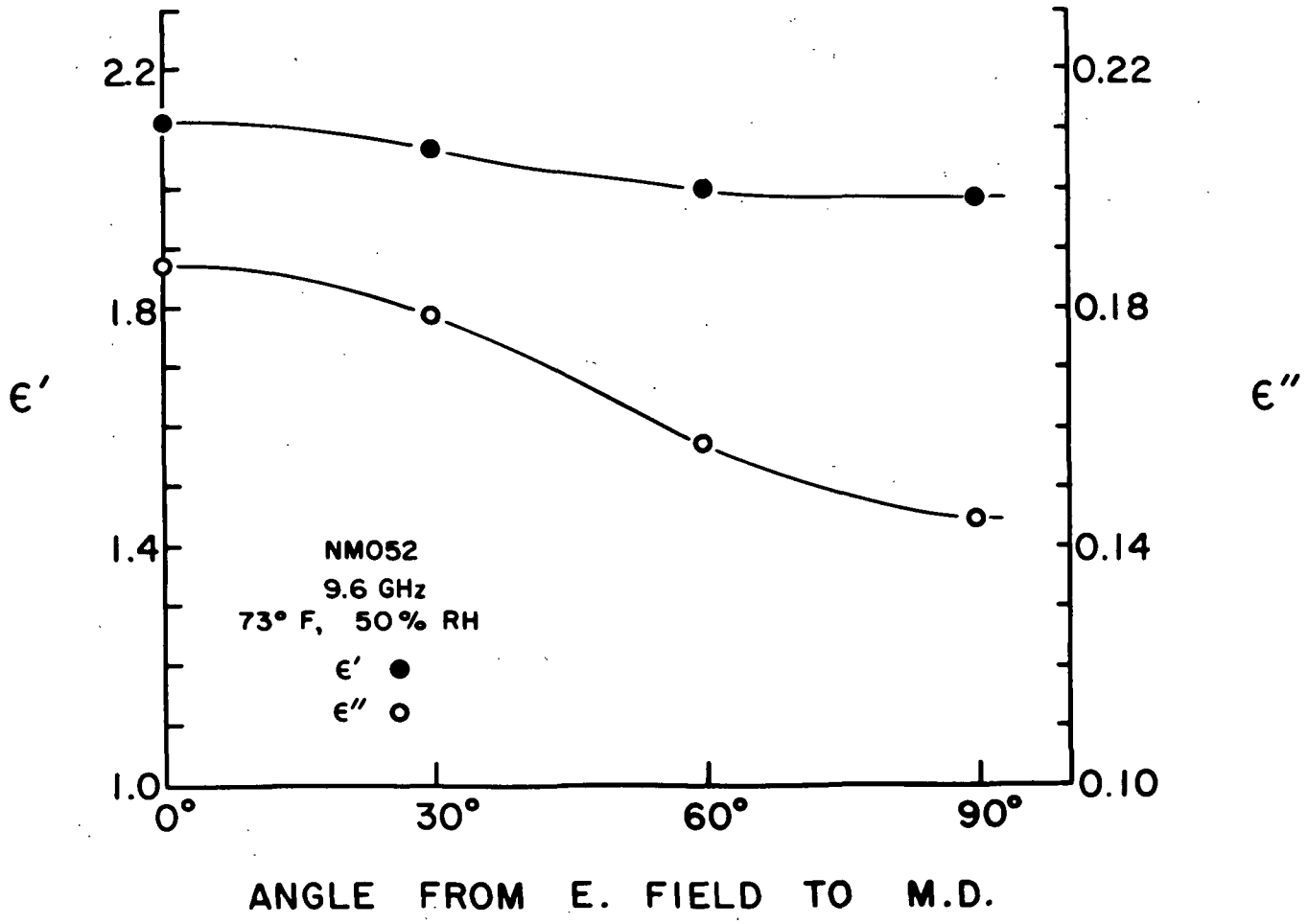

Fig. 5. In-plane dielectric anisotropy of a 45 g/m^2 machine-made newsprint.

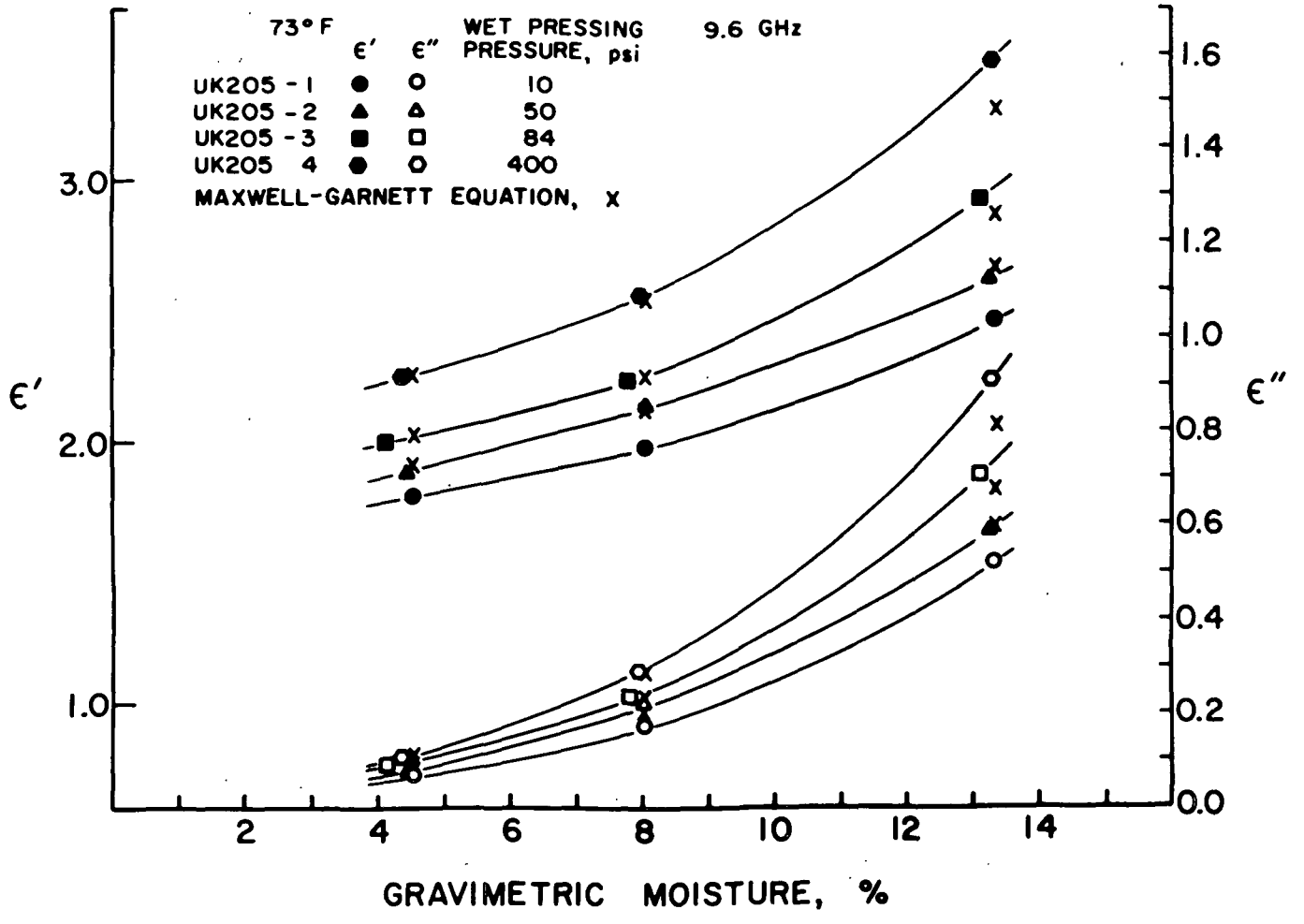

Fig. 6. The effect of wet pressing on the dielectric constant versus gravimetric moisture curve for an unbleached kraft sheet.

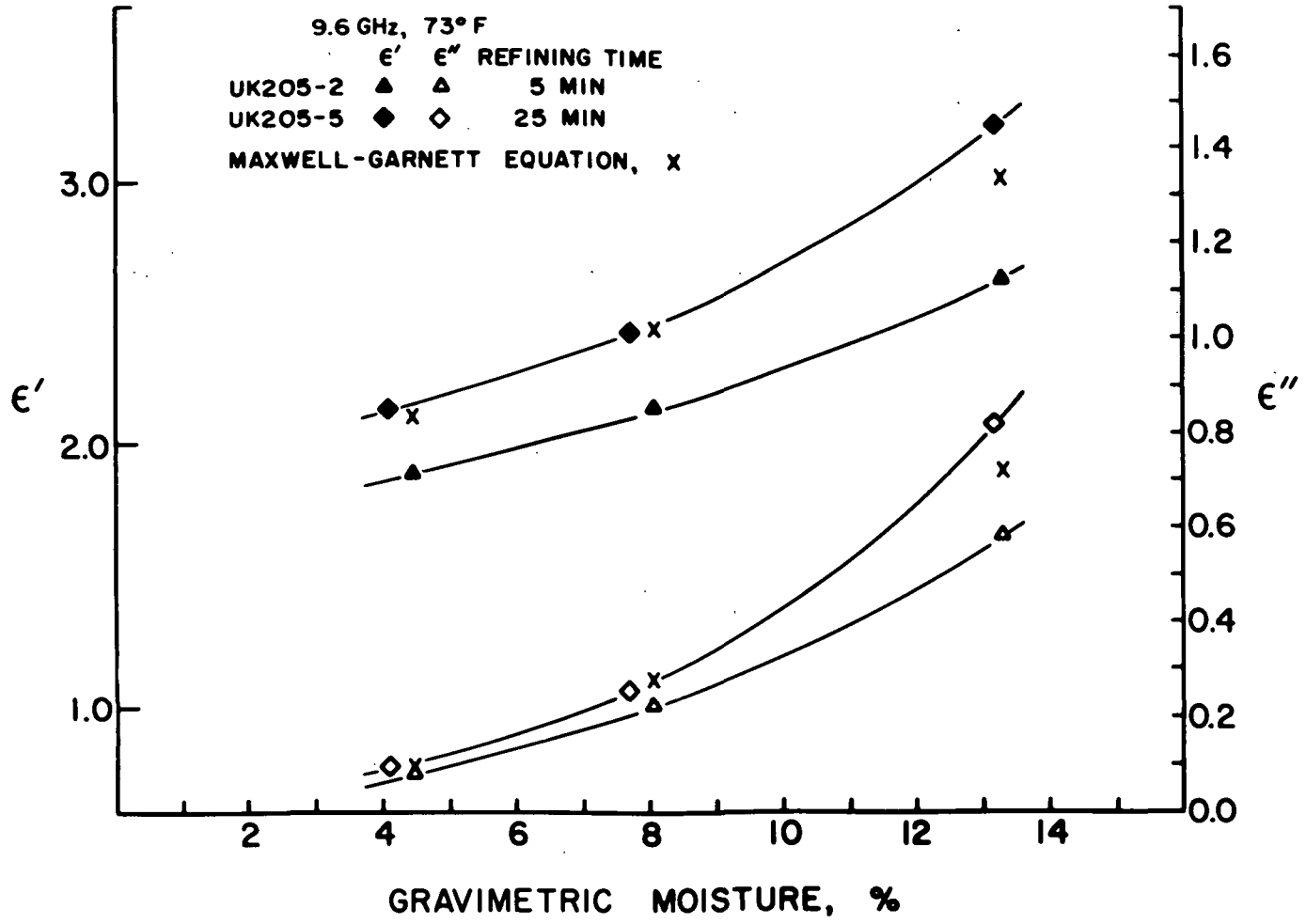

Fig. 7. The effect of refining on the dielectric constant versus gravimetric moisture curve for an unbleached kraft sheet.

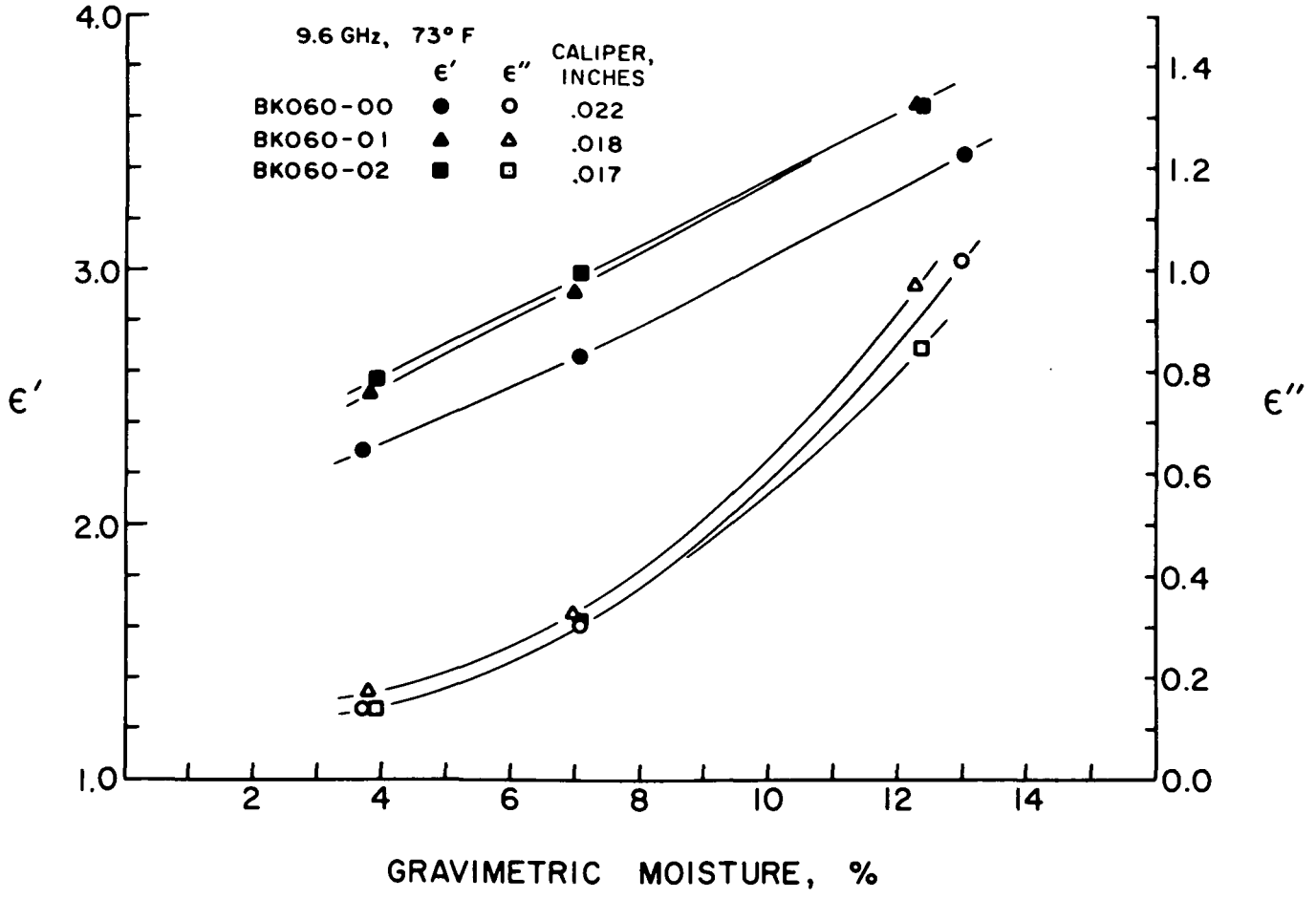

Fig. 8. The effect of calendering on the dielectric constant versus gravimetric moisture curve for a bleached kraft sheet.

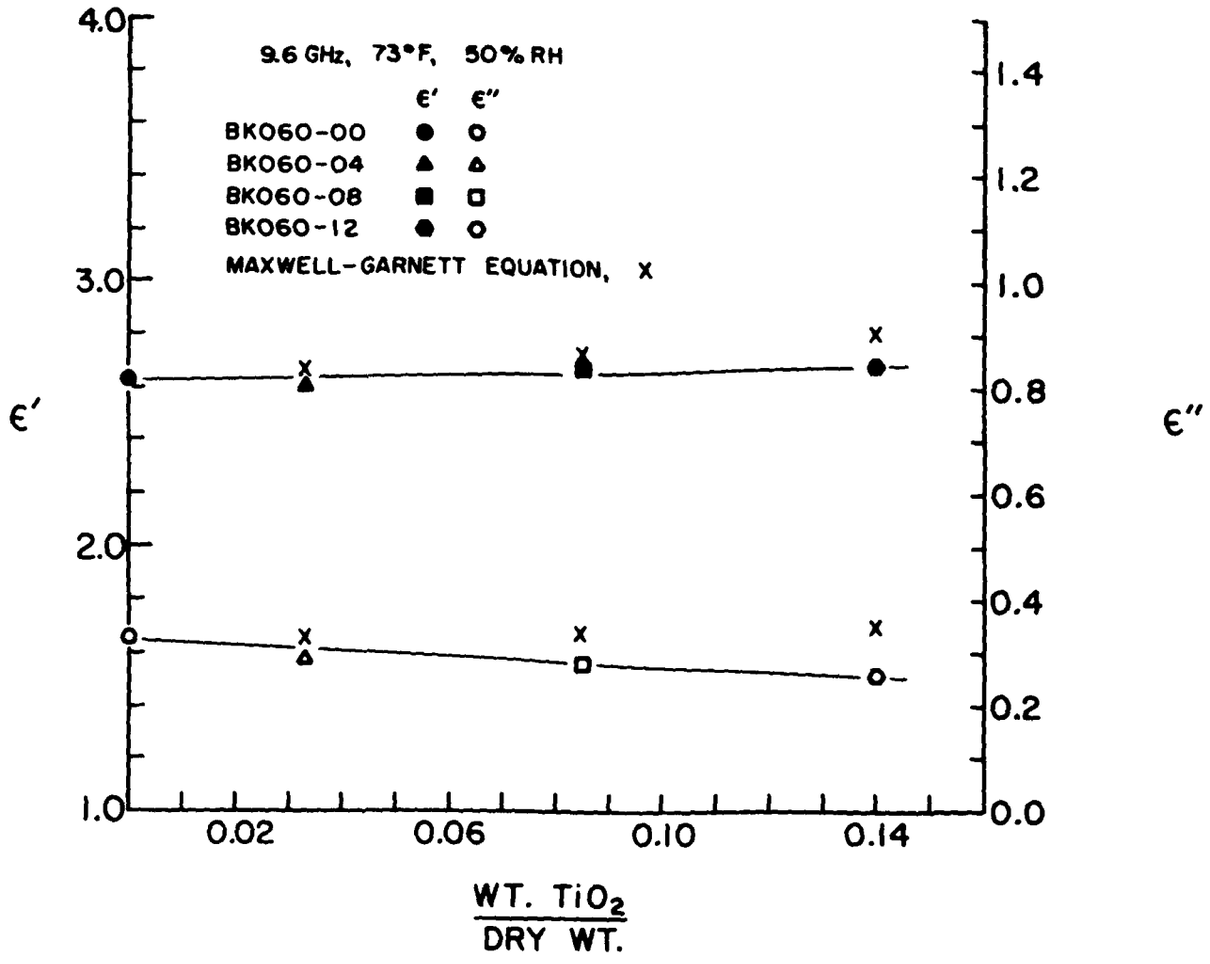

Fig. 9. The effect of TiO_2 addition on the dielectric constant of a bleached kraft sheet.